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(54) ULTRAVIOLET RAY ABSORBING GLASS

(57)Abstract:

PURPOSE: To obtain a glass capable of suppressing coloring of reflected light without lowering transmittance of visible light and excellent in heat radiation- reflecting property and useful for car, etc., by forming a specific intermediate film between an ultraviolet ray absorbing film and glass.

CONSTITUTION: The glass is obtained by forming an intermediate film having a refractive index of $(n_f \times n_g)^{1/2}$ which is a intermediate of a refractive index n_f of a ultraviolet ray absorbing film and a refractive index n_g of glass having a heat radiation-reflecting performance and simultaneously an optical film thickness of $\lambda/4$ wavelength of visible light having 400-700nm wavelength. between an ultraviolet ray absorbing film consisting essentially of one or more compounds among zinc oxide, titanium oxide and cerium oxide on the glass surface and the glass.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the ultraviolet absorbing glass which made the ultraviolet absorption film form in the glass surface.

[0002]

[Description of the Prior Art] It is important to cover the ultraviolet rays which carry out incidence to the interior of a room, in the car, etc. at the point it not only prevents suntan of the body, but that it can prevent deterioration of accessories the interior of a room and in the car etc.

[0003] Conventionally, as an ultraviolet ray absorbent, although the organic compound of **, such as a benzophenone and benzotriazol, was mainly known, these organic compounds had the trouble that deterioration tends to take place with absorption of ultraviolet rays.

[0004] Then, some methods of using as ultraviolet absorbing glass have been proposed by forming the film of inorganic compounds, such as a zinc oxide which has ultraviolet absorption nature, titanium oxide, and cerium oxide, on the surface of glass in that there is no deterioration.

[0005] Since the heat from sunlight raises an indoor temperature and reduces air conditioning effectiveness in a summer, in order to prevent this on the other hand, by making heat ray reflexivity give the object for automobiles, and the glass of *****, the invasion to the interior of a room of solar radiation is restricted, and raising air conditioning effectiveness is posing an important problem.

[0006] Although what is made to form coats, such as noble metals, and a conductive metallic oxide, a nitride, in the surface, and is obtained was in use as for current heat ray reflexivity glass, these thin films were lacking in ultraviolet absorption nature, and absorption of a visible ray was remarkable, and the trouble that it could not be used depending on a material also existed in the automobile or the part which needs the high visible-ray permeability of general *****.

[0007]

[Problem(s) to be Solved by the Invention] this invention tends to cancel the above-mentioned technical problem which the conventional technology had, and it has ultraviolet absorption nature and heat ray reflexivity, and it offers glass with high visible-ray permeability newly -- it aims at things.

[0008]

[Means for Solving the Problem] Ultraviolet absorbing glass characterized by forming an interlayer which this invention is made that the above-mentioned technical problem should be solved, and has a middle refractive index of a refractive index of an ultraviolet absorption film and a refractive index of glass between an ultraviolet absorption film and glass in ultraviolet absorbing glass with which a zinc oxide, titanium oxide, and an ultraviolet absorption film that uses at least one sort in cerium oxide as a principal component were formed in the glass surface, and has heat ray reflective engine performance is offered.

[0009] as an ultraviolet absorption film of this invention, a zinc oxide, titanium oxide, and a film that uses at least one sort in cerium oxide as a principal component mention -- having -- concrete -- ZnO, TiO₂, CeO₂, ZnO-TiO₂, ZnO-CeO₂, and TiO₂-CeO₂ Or ZnO-TiO₂-CeO₂ etc. -- from -- a becoming

film is mentioned and a component of further others can be included in these components.

[0010] It is $\text{CeO}_2\text{-TiO}_2$ among these. Since an ultraviolet absorption film of a system is excellent in an ultraviolet absorption property and excellent in a surface degree of hardness and chemical durability, it is desirable. However -- since there is a possibility of a film of this system having a very high refractive index, and causing reduction of light permeability from height of a reflection factor -- SiO_2 etc. -- it is desirable to add low refraction material and to make a refractive index as a film about into 1.9 to 2.1.

Thus, if the optical property of an interlayer which is made to reduce a refractive index of an ultraviolet absorption film, and is formed in the lower layer is cared about, especially since decline in light permeability is barred with high ultraviolet absorption engine performance maintained, it is desirable.

[0011] As a concrete presentation ratio (weight ratio) for providing effective ultraviolet absorption nature and high endurance, and making it a reflection factor not become high further, it is $\text{CeO}_2/\text{TiO}_2/\text{SiO}_2 = 1.0\text{-}5.0/1.0/0.5\text{-}1.5$, for example.

[0012] As for an ultraviolet absorption film of this invention, it is desirable to have 100nm or more thickness 800nm or less in consideration of ultraviolet absorption ability, permeability of the light, film reinforcement, etc.

[0013] In this invention, it is important for an interlayer to have a middle refractive index of a refractive index of an ultraviolet absorption film and a refractive index of glass.

[0014] If it thinks from a viewpoint of suppressing reflection of a visible ray and raising reflection in a near infrared ray field as a refractive index of an interlayer, especially a desirable thing is ng about a refractive index of nf and glass in a refractive index of nonreflective conditions, i.e., an ultraviolet absorption film. If it carries out, it is the refractive index nm of an interlayer. It is the case where an interlayer which has a refractive index which it carries out [refractive index] and forms $\text{nm} = (\text{nf} \times \text{ng})^{1/2}$ is formed. In addition, even if it is the refractive index of the range of $1/2^{**}10\%$ practically ($\text{nf} \times \text{ng}$), it does not interfere.

[0015] Although especially thickness of an interlayer is not limited, in order to stop color nonuniformity by thickness nonuniformity of an ultraviolet absorption film, as for the transparent membrane nm d which has $\lambda/4$ wave of optical thickness of a 400-700nm visible ray, i.e., optical thickness, (d is thickness), it is desirable that it is $\lambda_0/4$ (λ_0 is desired design wave length). In addition, practically, even if it is $\lambda_0/4$ optical thickness of $4^{**}10\%$ of range, it does not interfere.

[0016] In this case, if an interlayer is $\lambda/4$ wave of optical thickness of a visible ray, since nonreflective conditions will be satisfied about a visible ray, since amplitude (reinforcement) of the reflected light (R1) in an interface of an ultraviolet absorption film and an interlayer and the reflected light (R2) in an interface of an interlayer and glass becomes equal and a phase becomes reverse, R1 and R2 are decreased by composition, and a reflection factor falls. On the other hand, in a near infrared ray with wavelength longer than a visible ray, since nonreflective conditions stop satisfying and a phase gathers, R1 and R2 will be amplified by composition, and a reflection factor of this field becomes high as a result.

[0017] Moreover, if an interlayer is made to form on such conditions, since it becomes only reflection of an interface of air on the surface of the maximum, and an ultraviolet absorption film and looks substantially, reflection of a visible ray has the effect which also prevents coloring of the reflected light by interference of two or more interface reflection.

[0018] Moreover, a film on which the aforementioned optical property is satisfied as a structure of an interlayer of this invention, For example, SiO_2 , GeO_2 , aluminum 2O_3 , ZrO_2 , and TiO_2 , SnO_2 , In_2O_3 , Ta_2O_5 , ZnO , and CeO_2 etc. -- such mixture 2, for example, $\text{ZrO}_2\text{-SiO}_2$, etc. -- it not being limited at all especially as a material, if it is the included transparent membrane, but, if it thinks from a point of raising ultraviolet absorption ability further It is desirable that ultraviolet absorption nature oxides, such as a zinc oxide, titanium oxide, and cerium oxide, contain also in an interlayer. If an example is given concretely, ZnO-SiO_2 and $\text{ZnO-aluminum } 2\text{O}_3$, ZnO-GeO_2 , $\text{TiO}_2\text{-SiO}_2$, and $\text{TiO}_2\text{-aluminum } 2\text{O}_3$, $\text{TiO}_2\text{-GeO}_2$, $\text{CeO}_2\text{-SiO}_2$, $\text{CeO}_2\text{-aluminum } 2\text{O}_3$, and $\text{CeO}_2\text{-GeO}_2$ etc. -- the two-component system or these -- ZnO and TiO_2 And CeO_2 from -- it is 3 component system or a system of four or more components etc. which added one or more sorts of components chosen.

[0019] Furthermore, an electric conduction component can be added to an interlayer and heat ray reflexivity can also be raised to it. As these electric conduction component, they are Sb-SnO₂ and Sn-In₂O₃. Or aluminum-ZnO etc. can be mentioned.

[0020] in addition, a thing which carried out for example, thermal insulation ability (ratio of a difference of solar radiation permeability of glass, and light permeability) to having heat ray reflective engine performance in this invention one or more -- a table -- it is a thing the bottom.

[0021] Moreover, it can also be said by distributing an ultrafine particle of said electric conduction component in an interlayer, or forming an interlayer into an electric conduction film that heat ray reflective engine performance is raised.

[0022] Especially a formation method of an ultraviolet absorption film in this invention and an interlayer is not limited, and can be broadly chosen from dry process, such as a method conventionally used for coat formation, i.e., a vacuum deposition method, and the sputtering method and a CVD method, to wet methods, such as a sol gel process, evaporative decomposition, and a spreading thermal decomposition method.

[0023]

[Example] Although the example of this invention is given to below and being further explained to it, this invention is not limited to these. Evaluation of the film obtained in the following examples and examples of a comparison, Appearance (viewing), ultraviolet-rays permeability (Tuv:ISO -9050), visible-ray permeability (Tv:JIS-R3106), solar radiation permeability (TE:JIS-R3106), thermal insulation ability (the ratio of the difference of the solar radiation permeability of glass and light permeability, and $\Delta TE / \Delta TV$), and saturation ($C^* : 1/2$ in CIEL* $a^* b^* (a^{*2} + b^{*2})$) performed.

[0024] Mix example 1 1-propanol 22g, acetylacetone 7g, and 30g of cerium nitrates, it was made to dissolve, and one evening was agitated (A liquid). To 2-propanol 58g, 3.6g was mixed for 26g of A liquid, and ethyl silicate 40, 8.7g and 0.6g of 0.1N-hydrochloric-acid aqueous solutions were mixed for titanium acetylacetonate (Ti(OPr)₂ 2 (Acac)), and it considered as spreading liquid B. Sequential addition of 4.3g and the 3.0g of the 0.1N-hydrochloric-acid aqueous solutions could be carried out for 4.5g and tetra-isopropyl titanate at ethanol, ethyl silicate 40 was mixed, and it considered as spreading liquid C.

[0025] Spreading liquid C is applied with a spin coat method on soda lime glass ($n_g = 1.52$), and it calcinates for 30 minutes at 200 degrees C, and is TiO₂-SiO₂ of a refractive index 1.74 and 68nm of thickness. The interlayer (it is TiO₂:SiO₂ = 40/60 at a weight ratio) which consists of a transparent membrane of a system was obtained. Moreover, spreading liquid B is applied with a spin coat method, and it calcinates for 5 minutes at 600 degrees C, and is CeO₂-TiO₂-SiO₂. The ultraviolet absorption film (it is CeO₂:TiO₂:SiO₂ = 64/18/18 at a weight ratio) of a system was made to form. The refractive index of this ultraviolet absorption film was 2.05, and thickness was 180nm. The result of an optical property is shown in a table 1.

[0026] Sequential addition of ethyl silicate 40, tetra-isopropyl titanate, and the 0.2N-hydrochloric-acid aqueous solution may be carried out at example 2 ethanol, and it mixes, considers as the spreading liquid for interlayer formation, applies with a spin coat method on soda lime glass, it calcinates for 30 minutes at 200 degrees C, and is TiO₂-SiO₂ of a refractive index 1.72 and 75nm of thickness. The interlayer (it is TiO₂:SiO₂ = 38/62 at a weight ratio) which consists of a transparent membrane of a system was

[0027] Moreover, the cerium oxide colloid sol (Taki Chemical make: trade name need RARU U-15) was applied with the spin coat method, it calcinated for 30 minutes at 200 degrees C again, the ultraviolet absorption film was formed, and ultraviolet absorbing glass was obtained. The refractive index of a cerium oxide coat was 1.95, and thickness was 290nm. The property of the obtained ultraviolet absorbing glass is shown in a table 1.

[0028] Sequential addition of an ethyl silicate, a cerium nitrate, and the acetylacetone was carried out, and it considered as the spreading liquid for interlayers, and applied to example 3 ethanol with the spin coat method on soda lime glass, and the interlayer (it is CeO₂:SiO₂ = 40/60 at a weight ratio) which calcinates for 10 minutes at 400 degrees C, and consists of a transparent membrane of a refractive index 1.68 and CeO₂-SiO₂ system of 68nm of thickness was obtained. Moreover, zinc-oxide ultrafine particle

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CLAIMS

[Claim(s)]

[Claim 1] Ultraviolet absorbing glass characterized by forming an interlayer which has a middle refractive index of a refractive index of an ultraviolet absorption film, and a refractive index of glass, and has heat ray reflective engine performance between an ultraviolet absorption film and glass in ultraviolet absorbing glass with which a zinc oxide, titanium oxide, and an ultraviolet absorption film that uses at least one sort in cerium oxide as a principal component were formed in the glass surface.

[Claim 2] An interlayer is ng about a refractive index of nf and glass in a refractive index of an ultraviolet absorption film. If it carries out, it is the refractive index nm of an interlayer. Ultraviolet absorbing glass of claim 1 which carries out and is characterized by being the interlayer which forms nm $= (nf \times ng)^{1/2}$.

[Claim 3] An interlayer is ultraviolet absorbing glass of claims 1 or 2 characterized by having $\lambda/4$ wave of optical thickness of a 400-700nm visible ray.

[Claim 4] An interlayer is ultraviolet absorbing glass of any 1 term of claims 1-3 characterized by combining with heat ray reflective engine performance, and giving ultraviolet absorption ability including at least one sort in a zinc oxide, titanium oxide, and cerium oxide.

[Claim 5] An ultraviolet absorption film is ultraviolet absorbing glass of any 1 term of claims 1-4 characterized by consisting of cerium oxide, titanium oxide, and silicon oxide.

[Claim 6] An interlayer is ultraviolet absorbing glass of any 1 term of claims 1-5 characterized by raising heat ray reflexivity further by that cause including an electric conduction component.

[Translation done.]